Comparison of Activity of Ziegler-Natta Catalysts

prepared by recrystallization and chemical reaction methods towards polymerization of ethylene

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ABSTRACT

In the present study, Ziegler-Natta catalysts were prepared on supports that were synthesized via two different methods. The first method (method A) is called the recrystallization method, which employed $MgCl_2$ as a precursor. The second method (method B) is called chemical reaction method, which employed $Mg(OEt)_2$ as a precursor. The catalysts were characterized by XRD, TGA, ESR and nitrogen physisorption. BET specific surface areas of catalyst A and B were 123.1 and 142.2 m^2/g, respectively. Polymerization of ethylene was carried out over the catalyst and triethylaluminium. The catalyst prepared by method A exhibited higher activity than that prepared by method B. However, the properties of polymer obtained from both catalysts were similar. The results from XRD and TGA analyses confirmed that $Mg(OEt)_2$ was converted to $MgCl_2$.

KEYWORDS

Ziegler-Natta catalyst; Support catalyst; Ethylene Polymerization

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I . Introduction

Polyolefin such as polyethylene (PE) and polypropylene (PP) are major plastics in the world-wide polymer industry [1]. Therefore, the worldwide production volume of polyolefin has grown to more than 80 million tons per year until now and is predicted to rise continuously to exceed 140 million tons in 2010 [2].

Nowadays, tens of millions tons of polyethylene (PE) are being produced by Ziegler-Natta catalysts each year [3]. The Ziegler-Natta catalysts have been used for ethylene polymerization since 1950. Ziegler-Natta catalysts have advantages of producing product with high molecular weight, high melting point and controllable morphology. However the disadvantages of Ziegler-Natta catalysts are: (i) less control of growing polymer branching due to multiple metal sites of transition metal, (ii) encapsulation effect of polymer chains and (iii) difficulty of catalyst removal from the final product [4].

Many modern Ziegler-Natta catalysts for stereospecific olefin polymerization employ the high surface area support matrices for active transition metal catalyst sites. The first significant results were obtained in the early 1960s by using the reactive Mg compounds such as Mg(OH)Cl, hydroxylated MgO or $MgSO_4$. In the past 20 years, there have been many reports about the various supports for $TiC1_4$ catalysts including such magnesium compounds as MgO, $Mg(OH)_2$, $MgC1_2$, Grignard compounds, and Mg alkyl [5].

The manufacture of high-activity Ziegler-Natta catalysts for polymerizing ethylene requires a support that stabilizes the active centers of the catalysts. A variety of metal halides and oxides have been reported as suitable supports for the catalysts. Magnesium alkoxides were reported as efficient supports in some patents [5] and anhydrous $MgCl_2$ has been known as a preferred support for highly efficient Ziegler–Natta catalysts for the polymerization of olefins [6]. The best support is $MgCl_2$ due to the fact that Mg and Ti have similar atomic size and shape. Moreover, $MgCl_2$ has a similar crystalline structure to that of $TiCl_3$ [7].

Since the excellent properties of $MgCl_2$ supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of $MgCl_2$ have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between $MgCl_2$ and $TiCl_4$. These treatments are the ball-milling, the recrystallization methods and the chemical reaction [8]. The recrystallization method consists of a chemical activation by reaction of crystalline $MgCl_2$ with alcohol. For chemical reaction method procedure, the reaction between $TiCl_4$ and magnesium alkoxides such as $Mg(OEt)_2$ shows a very high activity for the polymerization of ethylene. During the reaction with $TiCl_4$, hydrocarbon solvents are incorporated and a reaction with $TiCl_4$ takes place in this layer to form $MgCl_2$ and $TiCl_{4-n}(OEt)_n$ compounds. Moreover, the catalyst synthesis procedure seems to be the most important factor for determining the catalyst performance since they give the final polymer with different properties.

In the present work, we have prepared two types of catalysts with different preparation procedures. For example, the first catalyst was synthesized by forming the adduct of $MgCl_2 \cdot EtOH$ and the second catalyst was prepared by using $Mg(OEt)_2$ as the starting material for support. The investigation was aimed at differentiating the nature of the catalyst obtained as well as their polymerization behaviors.

II. Experimental

2.1 Chemicals

Polymerization-grade ethylene and $AlEt_3$ (TEA) were donated from PTT Public Co.,Ltd. and Bangkok Polyethylene Co., Ltd., respectively. Diethyl aluminum chloride (DEAC) was donated from Tosoh Finechem, Japan, $TiCl_4$ and ethanol were purchased from Merck Ltd. Anhydrous $MgCl_2$ and anhydrous $Mg(OEt)_2$ were donated from Tosoh Finechem, Japan, n-heptane was purchased from Carlo Erba. n-Hexane and toluene was donated by Exxon Chemical Thailand Ltd. and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use. Ultra high purity argon (99.999%) was obtained from Thai Industrial Gas Co., Ltd. and was further purified by passing through molecular sieves 3 Å, BASF catalyst R3-11G, NaOH and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture.

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All operations were carried out under an inert atmosphere of argon using a vacuum atmosphere glove box and/or standard Schlenk techniques.

2.2 Catalyst preparation

2.2.1 $MgCl_2/TiCl_4$ catalyst: Catalyst A

$TiCl_4/MgCl_2$ catalyst was prepared by recrystallization method reacting $MgCl_2$-ethanol adduct with $TiCl_4$ in the following procedure: 2 g (0.0210 mol) of anhydrous magnesium dichloride was suspended in 100 ml of heptanes and 0.1259 mol of ethanol was added dropwise at room temperature. After the end of addition, the solution was stirred for 2 hours. Then 28 mol of aluminum compound was introduced dropwise and heated up to 90^{o}C and hold for 2 hours. Thereafter, 0.0255 mol of titanium tetrachloride was added and the mixture was stirred for 2 hours. Finally, the catalyst obtained was washed with heptane for several times.

2.2.2 $Mg(OEt)_2/TiCl_4$ catalyst: Catalyst B

In the current study, a monoester-type catalyst $TiCl_4/Mg(OEt)_2$ was prepared by a chemical reaction method without mechanical treatment (e.g. ball milling). $TiCl_4$ was reacted with a mixture of $Mg(OEt)_2$ in the following procedure: $Mg(OEt)_2$ 2.3 g (0.02 mol) and $TiCl_4$ 4 ml (0.036 mol) in toluene (96 ml) were heated up to 90℃ and hold for 2 hours. The mixture was washed with toluene and reacted again with $TiCl_4$ (4 ml) in toluene (96 ml) and then heated up to 90℃ and hold for 2 hours. Finally, the catalyst obtained was washed with hexane for several times.

2.3 Ethylene Polymerization

Ethylene polymerization was carried out in a 100-ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirred. The required amounts of hexane (30 ml), TEA, catalyst (Al/Ti molar ratio = 100) were added into the reactor. The reactor was then immersed in liquid nitrogen to freeze the solution and evacuated to remove argon. The reactor was heated to polymerization temperature (80^{o}C). Polymerization was stated by continuous feeding of ethylene. The pressure in the reactor was kept at 50 psi. Ethylene consumption was fixed at 18 mmole. The reaction time was recorded for the activity calculation. After the polymerization, the reaction was terminated by the addition of acidic methanol. The resulting polymer was then filtered off and dried in an oven at 60^{o}C for 6 h. The ethylene polymerizations ovine prepared by $Mg(OEt)_2/TiCl_4$ catalyst and $MgCl_2/TiCl_4$ catalyst with the same condition.

2.4 Characterization

X-ray diffraction (XRD) was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuKa (l = 1.54439 Å). The spectra were scanned at a rate of 2.4 min^{-1} in the range 2θ = 20–80^o.

Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q 600 analyzer. The samples of 10–20 mg and a temperature ramping from 298 to 873 K at 2 K min^{-1} were used in the analyzing process. The carrier gas was N_2 with UHP grade.

BET surface area of the samples after various pretreatments was performed to determine if the total surface area changes upon the various pretreatment conditions. It was determined using N_2 adsorption at 77 K in a Micromeritics ASAP 2010.

Melting temperatures and crystallinities of polymers were determined using differential scanning calorimetry, DSC (Perkin-Elmer DSC7), at a ramping rate of 10^{o}C min^{-1} in temperature range of 50–200 ^{o}C.

The electron spin resonance (ESR) spectra of catalyst samples were recorded at ambient temperature, with the use of JEOL JES-FE1XG spectrometer under N_2 atmosphere. The values of the g factor were determined against the Mn^{2+} standard.

Inductively coupled plasma (ICP) spectroscopy was used to determine the amount of titanium present in the catalyst precursors, using a Perkin- Elmer Plasma 1000 system.

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III. Results and discussion

In this study, two different catalyst preparation methods namely chemical reaction and recrystallization were synthesized and compared in order to clarify the correlation between their nature and polymerization behavior. As shown in Table 1, the Ti content incorporated in the final catalyst for both prepared catalyst was significant distinct influenced by the preparation procedure. However, the specific surface areas of the resulting catalysts were slightly different.XRD patterns represent the crystal structure of the $MgCl_2$ support and $Mg(OEt)_2$ supports as demonstrated in Figure 1. Anhydrous $MgCl_2$ has a cubic close packing (ccp) structure, which gives strong XRD patterns at $2\theta = 15^o$ (0 0 3 plane), 30^o (0 0 6 plane), 35^o (0 0 4 plane) and 50^o (1 1 0 plane) [9-10] and the paraffin film, which gives XRD peaks at $2\theta = 14^o$, 21^o and 24^o, was used to protect all samples from air. The literature from Giannini has reported that δ-$MgCl_2$, which provided disorder structure was the key factor for the active $MgCl_2$ [11]. For the magnesium ethoxide support, XRD patterns cannot be observed due to its highly dispersed form. The peaks of both supports are significantly different. The both supports were use to synthesize catalysts as shown in Figure 2. For $MgCl_2$ after treatment with $TiCl_4$, the peak intensity of XRD pattern of the recrystallized $MgCl_2$ decreased, while still gives similar pattern with those of anhydrous $MgCl_2$[9]. And for the $Mg(OEt)_2$ was prepared by the chemical reaction method, it has been already known that $Mg(OEt)_2$ is converted to $MgCl_2$ by reaction with $TiCl_4$. It was noticed that no characteristic peaks of $Mg(OEt)_2$ were presented in the XRD patterns of $Mg(OEt)_2/TiCl_4$ catalyst, namely, the original structure of $Mg(OEt)_2$ was destroyed by reaction with $TiCl_4$. $Mg(OEt)_2/TiCl_4$ catalyst shows a similar diffractogram to the activated $MgC1_2$. These results confirmed again that $Mg(OEt)_2$ is converted to $MgCl_2$ by reaction with $TiCl_4$ [5]. The XRD patterns of both catalysts are similar to $MgCl_2$ but the peak intensities are weaker. This result indicated that these two distinct procedures can result in the same catalyst crystal structure. TGA measurements were also performed to investigate the catalyst thermal stability (Figure 3 and Figure 4). The derivative weight curve clearly reflected the temperature at which the component was took away. A mass loss at less than 200^oC was attributed to the removal of $TiCl_4$ from the crystalline $MgCl_2$ matrix. And around 515 ^oC was due to the removal of electron donor as reported by Forte et al. . For our result, a weight loss for the removal $TiCl_4$ occurred around 200^oC and no weight loss around 515 ^oC was observed because electron donor was absent in our system. The both catalysts profiles are similar which assure again that $Mg(OEt)_2$ is converted to $MgCl_2$ by $TiCl_4$ reaction and match with similar XRD patterns of the both catalysts.

It is well known that three various titanium valences; Ti^{4+}, Ti^{3+} and Ti^{2+} are formed by reacting $TiCl_4$ with an alkylaluminium such as AlR_3 (R = alkyl group). Ti^{3+} species is considerably active for the polymerization of both ethylene and propylene while over-reduction of Ti^{3+} to Ti^{2+} leads to ethylene polymerization only [12, 13]. These transition metal oxidation states have been widely investigated through electron spin resonance (ESR) spectroscopy which is useful in detecting free radicals from paramagnetic solid materials. The ESR spectra of the catalyst solution from recrystallization and chemical reaction method are shown in Figure 5 It was noted that the amount of Ti^{3+} species could be obtained from relative intensity of a signal with a g-factor of 1.97 for recrystallization and chemical reaction methods, which was presented in two catalyst systems [14]. The recrystallization method can result in higher amount of Ti^{3+} more than the chemical reaction method. The titanium content from chemical reaction was higher than recrystallization method as shown in Table 1. The organoaluminum cocatalyst plays an important role in active site formation by alkylation and reduction of the titanium species. Then, the various Al/Ti ratios at 50, 100, 150, 200 and 250 were investigated to effect on the amount of Ti^{3+} for chemical reaction method as shown in Figure 6. The various Al/Ti ratios have slightly effect on the amount of Ti^{3+} from ESR spectra. The formation to active site (amount of Ti^3) between catalyst and cocatalyst was not high with Al/Ti ratio increase, and then recrystallization method has the amount of Ti^{3+} higher than chemical reaction method. For the next stage, ethylene polymerization was carried out. The catalytic activity and polymer thermal properties were reported in Table 2. The degree of crystallinity was calculated by comparison with heat of fusion (ΔH_f) of a perfectly crystalline polyethylene, i.e., 293 J/g. It was clearly seen that $MgCl_2/TiCl_4$ showed much higher catalyst activity than $Mg(OEt)_2/TiCl_4$ while there were no significant different for their melting temperature and degree of crystallinity as can be seen in Table 2. Normally, if the titanium content was high catalytic activity should be also high. However, for chemical reaction method, although, titanium content was high, the catalytic activity was low as shown in Table 1. The catalytic activity from chemical reaction was lower than recrystallization method because $Mg(OEt)_2$ was converted to $MgCl_2$, which transformed from alkyl group to Cl group. According to results of XRD and TGA confirmed again that $Mg(OEt)_2$ transformed to $MgCl_2$, thus probability of titanium was attached to support. The catalytic activity depended on active

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site of reaction. Catalyst reacted with cocatalyst to form active site, which was high contributed to highly activity. Chemical reaction method had more titanium attachment. Titanium might contribute to the attachment on inner and outer support [15]. When various Al/Ti ratios, spectra signals from ESR were not different led to no effect on Ti^{3+} as shown in Figure 6. Because catalyst reacted with cocatalyst to form active site, which formed at the outer support (surface), titanium attached inner support was more than outer support, thus probability of formation to active site in chemical reaction was low led to lower activity than recrystallzation method. The result of ESR confirmed that titanium attached inner support was more than outer support. The catalytic activity from chemical reaction was less than recrystallization method because overall titanium attached at surface led to more probability of formation to active site, which accorded with results of ESR. Figure 5 shows the ESR result of catalyst from two methods.

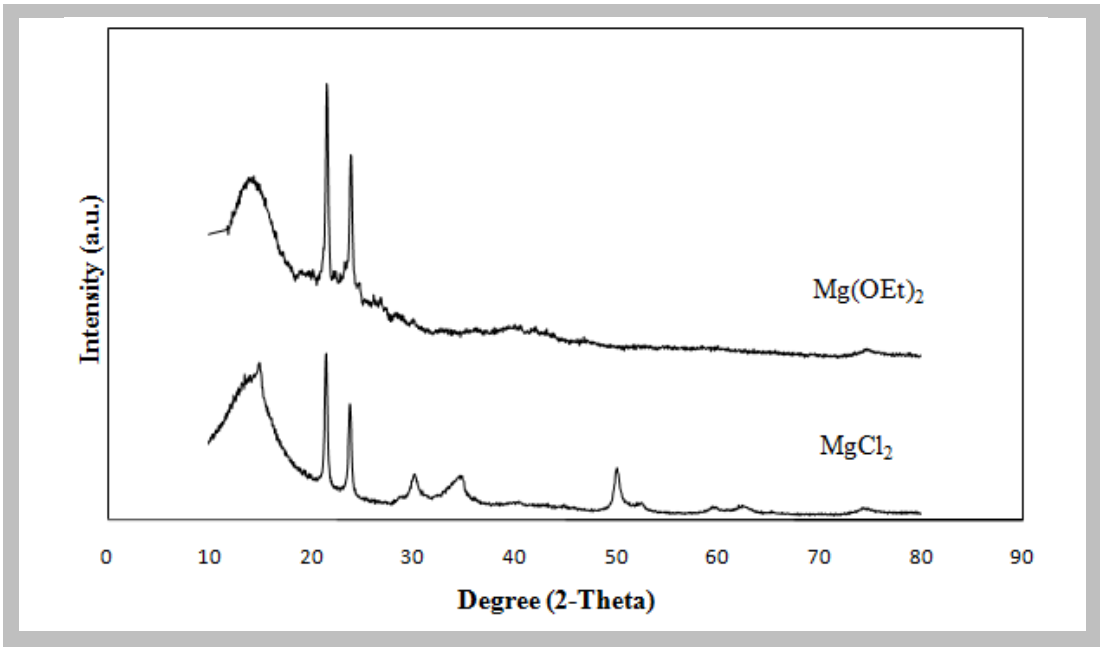

Figure 1
XRD patterns of different supports.

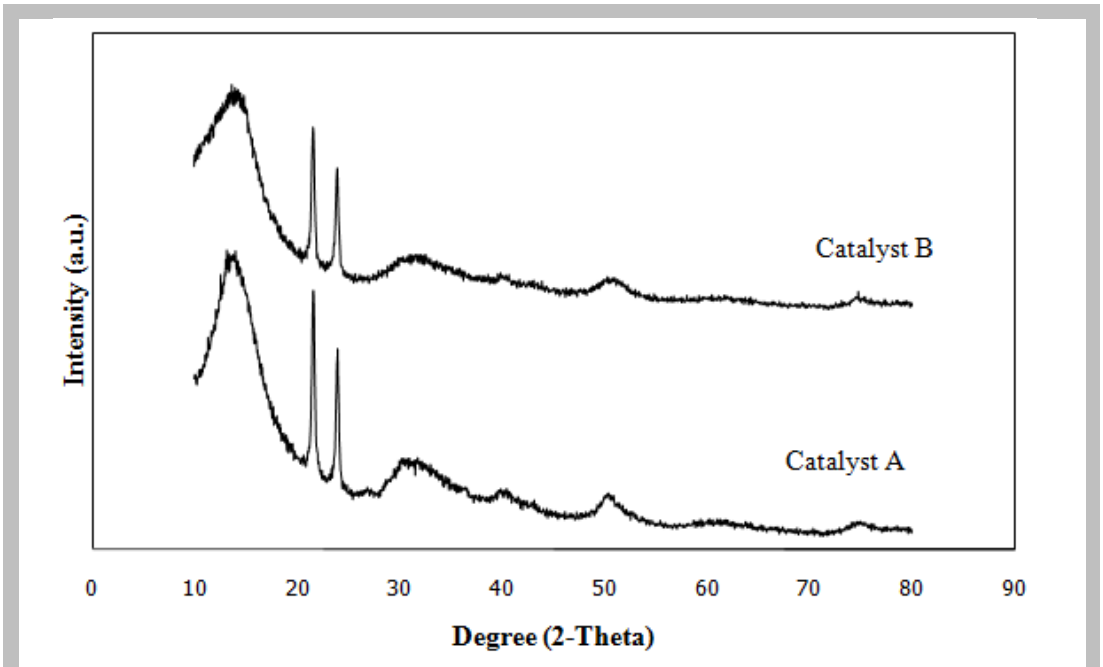

Figure 2
XRD patterns of different catalysts.

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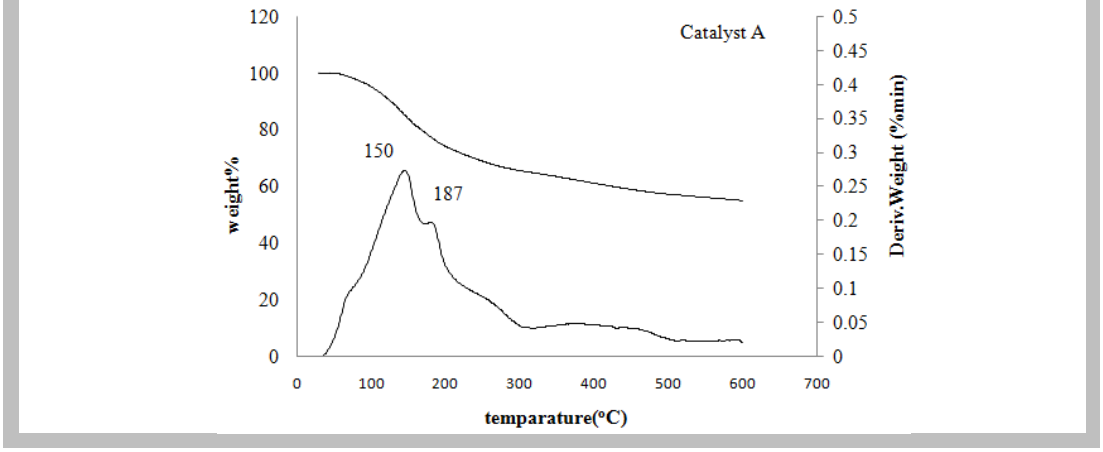

Figure 3
TGA profiles of Catalyst A.

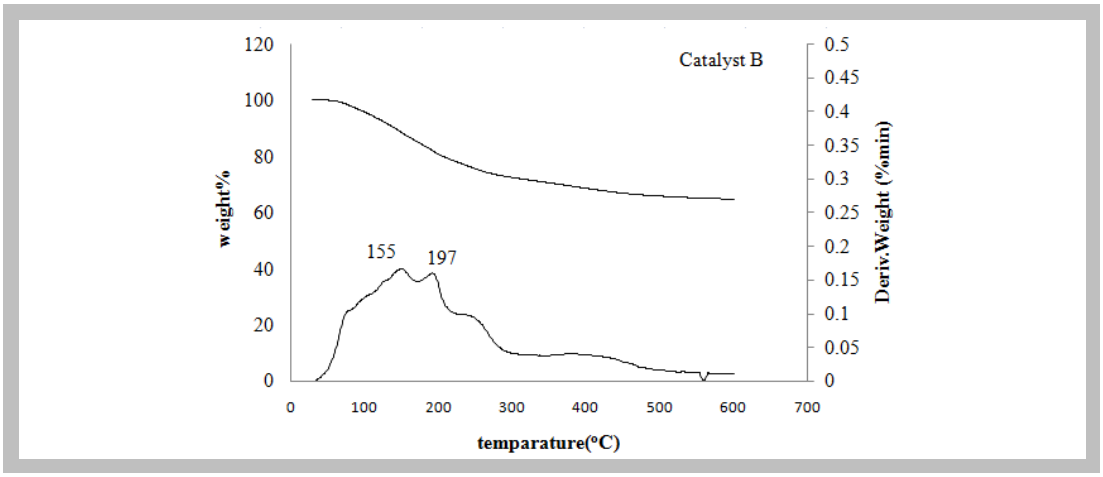

Figure 4
TGA profiles of Catalyst B.

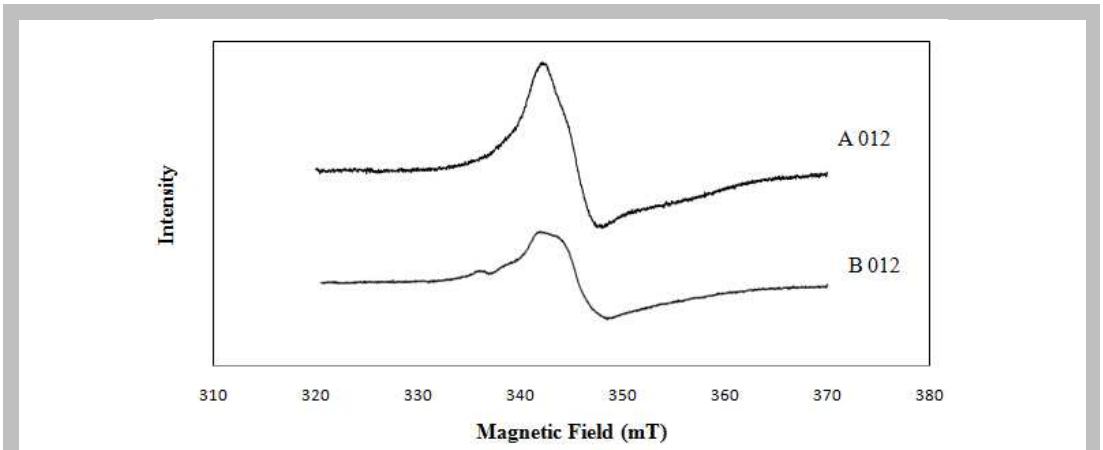

Figure 5
ESR spectra of the catalyst $TiCl_4/MgCl_2$ and $TiCl_4$/ $Mg(OEt)_2$ – TEA treated.

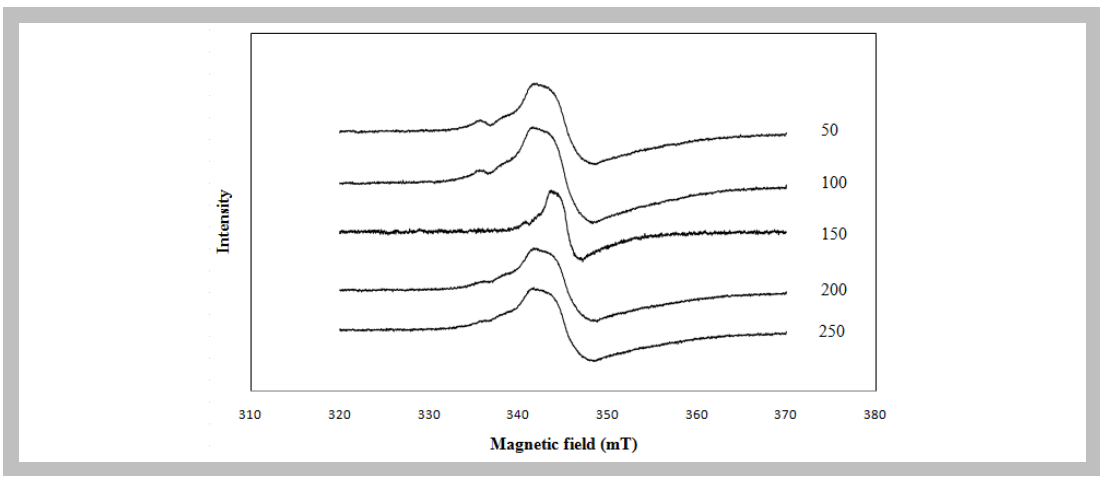

Figure 6
ESR spectra of catalyst by chemical reaction at different Al/Ti ratios.

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Table 1
BET specific surface area of catalysts

Catalyst	%Ti	specific surface area (m^2/g)
Catalyst A	3.09	123.1
Catalyst B	9.94	142.2

Table 2
Characterization of polyethylene obtained by different catalysts

catalyst	time(s) [a]	polymer yield [b] (g)	Activity[b] (kg-PE/mol Ti.h)	Tm (^oC)[c]	ΔHc (J/g)	Xc [c]
$MgCl_2/TiCl_4$	150	0.4669	1719	130.7	162.2	55.4
$Mg(OEt)_2/TiCl_4$	140	0.4455	551	130.0	160.5	54.8

[a] A period of time used for the total 0.018 mol of ethylene was consumed

[b] Polymerization condition: catalyst: 10 mg , cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n- heptane (30 ml), [ethylene=0.018 mol] , Temperature = 80 ^oC

[c] Obtained from DSC.

IV. Conclusions

Two different $MgCl_2$ precursors were employed to synthesize Ziegler-Natta catalysts via different preparation procedures. Catalyst A possessed a higher activity for polymerization of ethylene than catalyst B due to the higher Ti^{3+} content of catalyst A. Although the specific surface areas of both catalysts were similar, the titanium content of catalyst A was lower than that of catalyst B. The lower activity of catalyst B was a result of titanium being attached more to the inner support than outer support, thereby contributing less to the formation of active site during the activation process.

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REFERENCES

[1] He Fu-An, Zhang Li-Ming, F. Yang, Chen Li-Shan, and Q. Wu, "Polyethylene nanocomposites obtained from in-situ polymerization using supported Ziegler-Natta catalyst system," *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, vol. 44, pp. 11-15, 2007.

[2] P. Baum and J. Engelmann, *Nachrichten aus Chemie Technik und Laboratorium*, vol. 49, p. 359, 2001.

[3] K. Fukuda, B. Liu, H. Nakatani, I. Nishiyama, M. Yamahiro, and M. Terano, "Significant variation of molecular weight distribution (MWD) of polyethylene induced by different alkyl-Al co-catalysts using a novel surface functionalized SiO2-supported Ziegler-Natta catalyst," *Catalysis Communications*, vol. 4, pp. 657-662, 2003.

[4] P. Kaewarsa, "Polymerization of ethylene over the supported Ziegler-Natta and metallocene catalysts on magnesium hydroxide and magnesiuum hydroxychloriede," in *Thesis in Chemistry Science, Graduate School*: Khonkaen University, 2005.

[5] Dong-Ho Lee, Young-Tae Jeong, K. Soga, and T. Shiono, "Propylene polymerization with $Mg(OEt)_2$/benzoyl chloride/$TiCl_4$-triethyl aluminum/external donor catalyst systems," *Journal of Applied Polymer Science*, vol. 47, pp. 1449-1461, 1993.

[6] G. H. Zohuri, F. Azimfar, R. Jamjah, and S. Ahmadjo, "Polymerization of propylene using the high-activity Ziegler-Natta catalyst system SiO_2/$MgCl_2$ (ethoxide type)/$TiCl_4$/Di-n-butyl phthalate/triethylaluminum/dimethoxy methyl cyclohexyl silane," *Journal of Applied Polymer Science*, vol. 89, pp. 1177-1181, 2003.

[7] X. Cheng, "The use of functionalized zirconocenes as precursors to silica-supported zirconocene olefin polymerization catalysts." Faculty of the Virginia Polytechnic Institute and State University, Blacksburg, Virginia: VT Electronic Thesis and Dissertation Archive (United States), pp. 14-22, 2001.

[8] A. Parada, T. Rajmankina, and J. Chirinos, "Study of the MgCl2 recrystallization conditions on Ziegler-Natta catalyst properties," *Polymer Bulletin*, vol. 43, pp. 231-238, 1999.

[9] H. S. Cho and W. Y. Lee, "Synthesis of inorganic MgCl2-alcohol adduct via recrystallization method and its application in supported organometallic catalysts for the polymerization of ethylene with 1-hexene," *Journal of Molecular Catalysis A: Chemical*, vol. 191, pp. 155-165, 2003.

[10] K. Norio "The discovery and progress of $MgCl_2$-supported $TiCl_4$ catalysts," *Journal of Polymer Science Part A: Polymer Chemistry*, vol. 42, pp. 1-8, 2004.

[11] U. Giannini, "Polymerization of olefins with high activity catalysts," *Die Makromolekulare Chemie*, vol. 5, pp. 216-229, 1981.

[12] N. Kashiwa and J. Yoshitake, "The influence of the valence state of titanium in $MgCl_2$-supported titanium catalysts on olefin polymerization," *Die Makromolekulare Chemie*, vol. 185, pp. 1133-1138, 1984.

[13] K. Soga and M. Terano, "Preparation of highly active supported catalysts for producing polypropylene with less content of chloride," *Polymer Bulletin*, vol. 4, pp. 39-44, 1981.

[14] V. A. Zakharov, S. I. Makhtarulin, V. A. Poluboyarov, and V. F. Anufrienko, "Study of the state of titanium ions and the composition of the active component in titanium-magnesium catalysts for ethylene polymerization," *Die Makromolekulare Chemie*, vol. 185, pp. 1781-1793, 1984.

[15] K. Tangjituabun, "Effect of external agents on the activation and deactivation of Ziegler-Natta catalyst for propylene polymerization," in *Docter's Thesis, Chemical Engineering, Graduate School*: Chulalongkorn University, 2008.